

INVESTIGATION OF ORGANIC SULFUR STRUCTURE
AS A FUNCTION OF COAL RANK

S.Mitra, F.E.Huggins, N.Shah, and G.P.Huffman
Consortium for Fossil Fuel Liquefaction Science
University of Kentucky, Lexington, KY 40506-0107

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INTRODUCTION

X-Ray Absorption Fine Structure (XAFS) spectroscopy is proving to be a very promising method by which information on the electronic bonding state and atomic environment of dilute elements in complex samples can be readily obtained. Of especial importance to coal science, is the technique's demonstrated ability to provide detailed information on organic sulfur in coal^{1,5}. In this paper, we present the results of an XAFS investigation into the occurrence of various forms of sulfur present in a series of coals and maceral separates of different ranks.

EXPERIMENTAL PROCEDURE

Samples were selected for this study on the basis that they contain predominantly organic sulfur. A large number of the samples were maceral separates prepared by density gradient centrifugation (DGC), which effectively removed inorganic sulfur forms. A detailed description of the DGC methods can be found elsewhere^{6,8}. Other samples were whole coals or coal extracts with very little inorganic sulfur contents. Samples were prepared for XAFS spectroscopy by grinding representative samples to less than 100 mesh. The samples were then cold-pressed into pellets of boric acid of approximately 2.5 cm diameter or placed in thin Mylar bags for the XAFS experiments.

Some of the sulfur K-edge XAFS measurements on the coals were performed at the Stanford Synchrotron Radiation Laboratory on wiggler beam-lines VII-3 and IV-1. Electron energies were 3.0 and 3.3 GeV and beam currents were typically in the range 40 to 80 mA. Other XAFS measurements were conducted at the National Synchrotron Light Source at Brookhaven National Laboratory on beam-line X19-A, with electron energies 2.53 GeV and beam currents 90-200 mA. At both synchrotron facilities, Si (111) double crystal monochromators were used to vary the X-ray energy from about 100 eV below to as much as 600 eV above the sulfur K-shell absorption energy (2472 eV). An all-helium pathway was used to minimize absorption of the X-rays. Thin Mylar windows (6 μ m) were also used for the same reason. Fluorescent experiments were performed for this study with a Stern-Heald type detector.

Complementary studies with Mössbauer and X-Ray Photoelectron spectroscopies (XPS) were also performed on some of the samples to ascertain the amounts of pyritic sulfur, iron sulfates, and oxygen-bonded sulfur compounds that might be present in the samples.

RESULTS AND DISCUSSION

The XAFS structure can be divided into two regions: the near edge structure, known as XANES, within about ± 30 eV of the edge, and the extended region, the EXAFS, from about 30 eV to 300-400 eV above the edge. The XANES region of the spectrum provides information on the

bonding and oxidation state of the sulfur atoms. The EXAFS region, on the other hand, gives information about the local structural environment of the atoms.

In this study, we have concentrated on the XANES region of the spectra. The XANES structure typically consists of one or more peaks superimposed upon an absorption step. The peaks in the XANES region are derived either from transitions to vacant, bound levels, or from low energy scattering resonances. The first large peak in the XANES of all sulfur compounds, the white line, arises from the electronic transition from the 1s level to vacant np, or ns levels. A least-squares analysis of the XANES structure can be made by fitting the data to the sum of an arctangent edge step, which represents the transition of the photoelectron to the continuum, and a number of lorentzian peaks, which represent transitions to vacant bound states or scattering resonances. Each different sulfur compound exhibits one or more peaks and an edge step. Hence, the sulfur K edge of a coal sample that has a number of distinct organic sulfur forms, should exhibit a number of 1s to np/ns transitions and a corresponding number of transitions to the continuum. In practice, however, we have found that in the least-squares analysis at most only two arctangent steps are needed to obtain an adequate fit. The lower energy step represents the transition to the continuum for the sulfur bonded to carbon and the other step represents the corresponding transition for sulfur bonded to oxygen. The relative areas under the peaks can then be used in a semi-quantitative manner to show the variation of organic sulfur forms from sample to sample. However, it should be emphasized that there is at present no direct relationship between peak area and the abundance of a given organic form of sulfur, because of our lack of knowledge concerning transition moments, selection rules, etc. for the transitions in different sulfur compounds. Such relationships remain to be established in future work.

In the analysis procedure, the zero point of energy for the sulfur XANES spectra is defined as the major peak in the differential of the elemental sulfur spectrum. Relative to this point, pyritic sulfur has its white line at about 1.5 eV, and organic sulfides, such as dibenzyl sulfide, have white lines at about 2.2 eV. Thiophenic sulfur compounds, such as dibenzothiophene, have their major peaks at about 2.8 eV. Among sulfur-oxygen compounds, organic sulfoxides and sulfones have white lines at about 4.9 and 9.9 eV, respectively, whereas inorganic sulfates have white lines at around 11.4 eV. The edge step for these different compounds also exhibit similar displacements. The positive shift with increasing sulfur oxidation state is because of decreased screening of the nuclear charge for the 1s level electrons as valence electrons are transferred to the oxygen anions. In various coal spectra, fitted peaks at about the correct positions can be associated with all the sulfur forms listed above.

Coals and maceral separates of high rank appear to have little or no sulfur-oxygen bound components and the relatively small peak at 8-12 eV is believed to be principally a scattering resonance^{9,10}. Such samples were fit with only one arctangent function, as shown in Figure 1. Other samples, principally of lower rank, did need a second step for a better fit and exhibited a much larger peak at 8-12 eV, as shown by the XANES spectrum of leonardite in Figure 2. Virtually all of the sulfur in this sample is thought to be organic as all common inorganic forms-of-sulfur, namely pyrite, iron sulfates, and gypsum, were not detected by iron Mössbauer spectroscopy or calcium K-edge XAFS spectroscopy.

A tabulation of the areas under the different peaks for the samples examined in this study is shown in Table 1. Weight percent carbon (dry, ash-free) from ultimate analyses is used as an approximate measure of the rank of the coals. A systematic variation with coal rank is found in the relative amounts of higher energy peaks compared to the lower energy peak components. The lower rank coals show very pronounced peaks at 8-12 eV, suggestive of the increasing amounts of sulfur-oxygen forms, and the percentages of the areas under these peaks are considerably higher, as shown in Table 1. Figure 3 shows how the peak intensities vary for three coals of different ranks.

CONCLUSIONS

The sulfur K-edge XANES data obtained to date on coals of low inorganic sulfur abundances show a variation in both type and abundance of organic sulfur forms that was not expected. Low-rank coals appear to contain appreciable amounts of sulfur-oxygen compounds and such compounds appear to increase relative to sulfides and thiophenes as rank decreases. It should be emphasized that the percentages quoted in Table 1 are merely for areas under peaks in the least-squares fit. It remains to be established what the relationship is between peak areas and abundances for the different sulfur species and further studies are planned towards this end.

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Table 1. XANES peak areas for various coals investigated.

Sample	%C, daf Whole Coal	% Area of Xanes peaks					
		1	2	3	4	5	6
PSOC 733, WV							
Exinite	87.4	0	60	20	6	14	0
Vitrinite	87.4	0	49	22	9	20	0
Inertinite	87.4	0	52	14	7	27	0
UKCAER 71155, KY							
Vitrinite	84.2	5	48	23	17	5	0
OHIO #5							
Vitrinite	83.5	4	52	20	5	20	0
OHIO #6							
Vitrinite	83.5	0	62	17	16	6	0
UKCAER 91864, KY							
NMP Extract	82.2	4	59	17	6	13	0
UKCAER 71094, KY							
Vitrinite	80.0	6	44	22	15	13	0
Inertinite	80.0	11	41	15	9	24	0
Exinite	80.0	5	44	24	17	10	0
Coal	80.0	7	46	26	11	11	0
PSOC 1110, Utah							
Exinite	72.5	10	30	13	25	14	8
Vitrinite	72.5	10	27	13	31	14	5
PSOC 1108, Utah							
Vitrinite	68.0	5	25	11	30	20	9
Leonardite							
Sample-A	60.1	4	23	21	39	11	2
Sample-B	60.0	5	20	18	24	33	0

Peaks occur in the following energy ranges:

Peak 1: 1.0- 2.2 eV, Peak 2: 2.0- 3.1 eV, Peak 3: 4.5- 4.9 eV,
Peak 4: 9.3-10.3 eV, Peak 5: 11.5-12.0 eV, Peak 6: 15.0-17.5 eV.

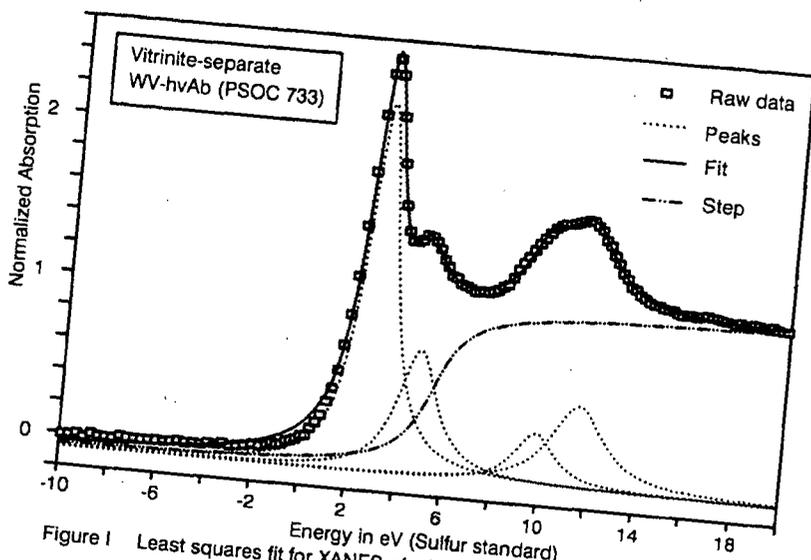


Figure 1 Least squares fit for XANES of a higher rank coal maceral with one step

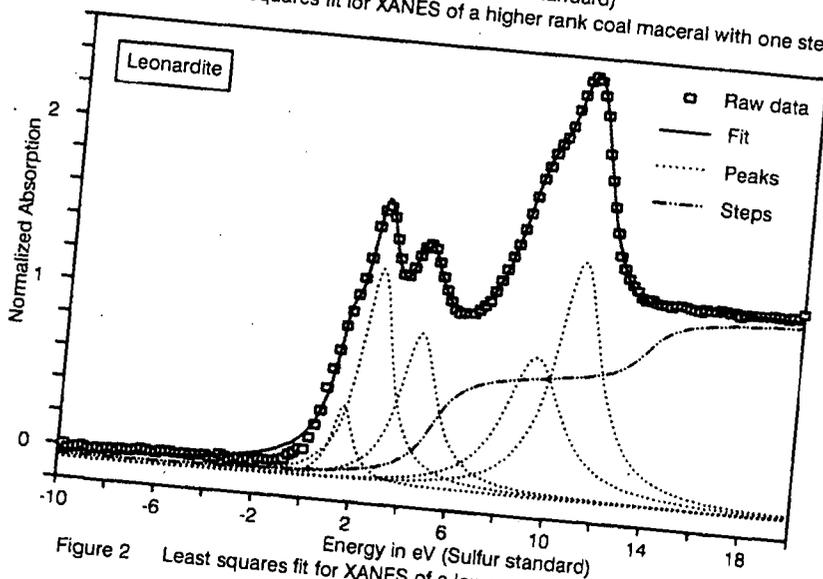


Figure 2 Least squares fit for XANES of a lower rank coal with two steps

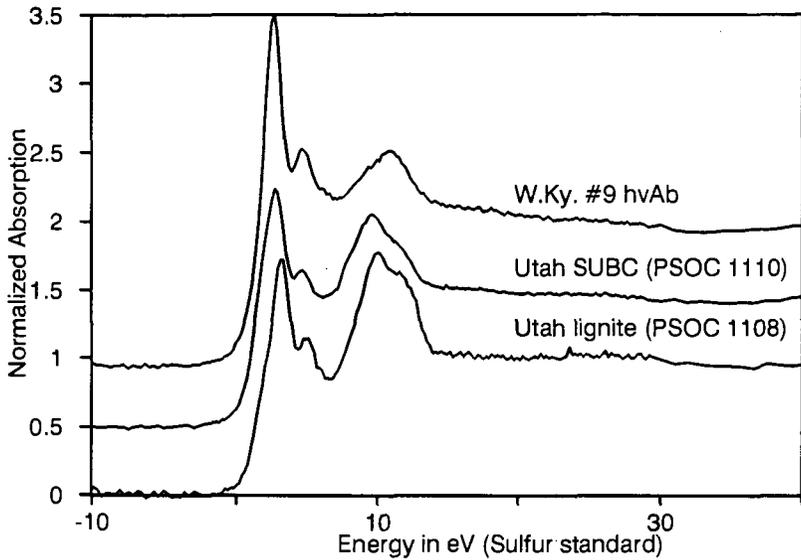


Figure 3 Sulfur XANES of coals of different ranks